

Direct and High-Resolution Measurements of Retardation and Transport in Whole Rock Samples under Unsaturated Conditions

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Evaluation of chemical sorption and transport is very important in the investigations of contaminant remediation, risk assessment, and waste disposal (e.g., the potential high-level nuclear waste repository at Yucca Mountain, Nevada). Characterization of transport parameters for whole rock samples has typically been performed in batch systems with arbitrary grain sizes and a high water/rock ratio. Measurement of these parameters under conditions more representative of fractured rocks *in situ* provides a better understanding of the processes occurring there.

The effective K_d approach has been commonly employed to quantify the extent of contaminant-medium-fluid interactions. Unrepresentative K_d values will lead to unrealistic assessments of contaminant transport. Experimentally determined K_d values are predominantly obtained from batch experiments under saturated and well-mixed conditions. Batch-sorption experiments can be problematic because: (1) saturated conditions with large water/rock ratios are not representative of the *in situ* vadose condition, and (2) crushed rock samples are used, with the sample size (in the range of microns to sub-millimeters) chosen more or less arbitrarily and mainly for experimental convenience, and (3) for weakly sorbing contaminants, a batch-sorption approach can yield variable and even negative K_d values, because of the inherent methodology of calculating the K_d values by subtracting two large numbers (i.e., initial and final aqueous concentration).

In this work, we use an unsaturated transport-sorption approach to quantify the sorption behavior of contaminants and evaluate the applicability of the conventional batch-sorption approach in unsaturated rock. Transient experiments are designed to investigate water imbibition and chemical transport into the rock sample (with size in the centimeter range) by contacting one end of a sample with water containing chemical tracers. Capillary-driven imbibition transports chemicals farther away from the source. Sorbing chemicals will be subjected to retardation that leads to delayed transport (compared to nonsorbing chemicals). This approach enables us to investigate the contaminant-medium-fluid system with weak (yet nonzero) sorption. Two profiling techniques, rock drilling (with a sampling interval of 1 mm) and laser ablation-inductively coupled plasma-mass spectrometry (with a spatial resolution of ~20 microns), have been developed to measure chemical concentration as a function of distance in the sample. The results shows that K_d values for sorbing chemicals (e.g., lithium, and cesium) are consistently much lower (~3-7 times) than the data from the batch-sorption approaches reported in the literature. This new approach generates more realistic sorption data (under unsaturated transport conditions) for flow and transport modeling.